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A CORRELATION OF STEPWISE STABILITY CONSTANT RATIOS AND SOME STRUCTURAL AND BONDING PROPERTIES OF TRANSITION METAL AND ZINC COMPLEXES

by

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ABSTRACT

Stepwise stability constant ratios for some transition metal and zinc amino acid and halide complexes are analysed. It is shown that the observed ratios for Cu, Ni, and Co amino acid complexes are larger than the calculated ratios by a factor R, the Bjerrum rest effect. It is suggested that the rest effect is due to metal-nitrogen covalency, there being sufficient transfer of charge from ligand to metal in the first association stage to reduce markedly the electrostatic attraction between ligand and metal in the second.

In the second part of the paper, it is shown that the structural transition from octahedron (hexahydrated cation) to tetrahedron (MX_4, where X = halide) occurs in the first ion association stage for Zn, Co, and Mn chlorides, and in the second or subsequent stages for Zn bromide. As expected, the ratios for Ni chloride indicate octahedral bonding. The 1:4 Cu:Cl species would seem to be 4-coordinate.

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INTRODUCTION

The absolute magnitudes of stepwise stability constants for metal–ligand ion association reactions are useful in choosing the ligands that might be of application in, e. g. the ion-exchange separation of rare-earths. However, the stability constants often do not tell us the nature of the species formed. In an earlier publication in this series (1), the ratios of stepwise stability constants for some simple rare-earth and cupric ion association systems were analysed using the Bjerrum relationship (2)

$$P = b_1 : b_2 = S \times T \times R,$$

where b_1 and b_2 are stepwise stability constants defined by

$$b_n = \left[ML_n\right] \Big/ \left[ML_{n-1}\right] \left[L\right]$$

where M = metal ion and L = ligand. The S, T, and R factors are:

S factor: S is purely statistical and can be evaluated from a knowledge of the number of available cation sites and ligand groups. For a bidentate ligand binding to a hexahydrated cation (octahedral), $S = 2 \times 12/5 = 4.8$. The factor 2 arises because the probability of a ligand's leaving the 1:2 associate is twice that of the ligand's leaving the 1:1

T factor: This factor is a measure of the work done in bringing a second ligand from infinity to its equilibrium position in the 1:2 (metal:ligand) associate against the repulsive force exerted by the

already bound ligand. Therefore, T, being electrostatic in nature, should be independent of the nature of cation and ligand. Table I lists T values derived from experimental P values for rare-earth, cupric, and zinc ion association systems. The characterization of certain metal–ligand systems by a given T value would aid considerably in the interpretation of the vast compilations of stability constants, e.g. the Chemical Society publications (3). One of the aims of this work is the analysis of stepwise stability constant ratios for transition metal–amino acid and –halide complexes in order to determine whether a T value = 1.6 holds for these singly-charged ligand systems. The simpler ligands have been studied so as to minimize steric hindrance effects and long-chain hydrocarbon interactions with the water structure. The latter effect could introduce important entropy changes.

R factor: R, the rest effect, covers those effects that are neither electrostatic nor statistical. Bjerrum (2) defined R as "the influence of bound ligands on the binding power of the metal ion". In this paper, it is demonstrated that rest effects are present in transition metal–amino acid complexes, and the significance of the R term is discussed.

The transition metal and zinc ions in aqueous solution are hexahydrated, with octahedral or distorted octahedral structures. The 1:4 halide complexes are, in some instances, tetrahedral (e.g. Co). In the second part of this paper, P values for two or more stages of metal–halide ion association are analysed, so that the stage of ion association at which the structural change (octahedral ⟶ tetrahedral) occurs may be determined.

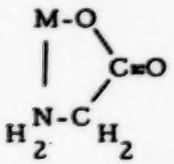
DISCUSSION

The possible reactions between a cation and a simple (primary amino) amino acid (e.g. glycine) may be formulated as follows (4),

$$M + NH_2CH_2COO = M\text{-}O.CO.CH_2.NH_2 \quad (a)$$

$$\text{or} \quad M\text{-}NH_2.CH_2.COO \quad (b)$$

or



(c)

The (primary amino) amino acids are generally regarded as being bidentate ligands (4), and this may be readily confirmed from the magnitudes of the observed P values. The above reactions are analagous to monodentate and bidentate glycolate interaction with Cu, Zn, and the rare-earths, so that a T value = 1.6 (Table I) may be postulated for reactions (a), (b) and (c). The S factors for reactions (a), (b), and (c) are 2.4 (= 2 x 6/5), 2.4 and 4.8 respectively for a cation with six equivalent binding sites. The corresponding P (calc.) values are, therefore, 3.8, 3.8 and 7.7. In Table II are presented the observed and calculated P values for some (primary amino) amino acid complexes of Cu, Ni, Co, Fe, Mn, and Zn. The P(calc.) and P(obs.) values for Zn are in excellent agreement, indicating that a T value = 1.6 holds for this system and that the ligands are bidentate. The data for Mn and Fe glycine complexes are too few for any unequivocal conclusions to be drawn, but the P(obs.) values would tend

to favour bidentate ligandcy. For the leucine and valine complexes of Mn, P(obs.) < S. Consequently, the latter systems would seem to warrant investigation.

It was shown in an earlier publication (1) that T = 1.1. for singly-charged ligands (e.g. chloride) ion pairing with the rare-earth hydration sheath. When this T value was corrected for the smaller separation of ligands in a complex, then T (monovalent ligand complexing) ~ 1.4, a value in good agreement with the directly derived T values listed in Table I. It would seem, therefore, that the metal-oxygen bonding in the complexes listed in Table I is of low covalent character, i.e., mainly ionic. This conclusion has also been reached by Jones (20) and more recently by Moeller and coworkers (21). It is very likely, therefore, that the Zn-O bond and the Zn-N bond in the presently studied system are of low covalent character.

The observed P values for the Cu, Co, and Ni complexes indicate that the value of R is appreciable (Table III). These cations form much stronger complexes with the (primary amino) amino acids than does Zn, showing that the ligands are probably bidentate. The S values for Cu have been computed on the basis of four available cation sites. The Jahn-Teller effect was shown to be operative in the cupric–glycolate and –acetate systems (1), and the effect has also been observed in the Cu–ethylenediamine system (22). Furthermore, the log b values for the three stages of Cu–glycine association (6) are 8.22, 6.97 and <1, while the corresponding figures for Co (6) are 4.61, 3.75 and 2.56.

The T value = 1.6 for singly-charged ligand systems covers contributions to the magnitude of P from, e.g. preferential disruption of the hydration sheath in a given stage of ion association and also any solvent structure and dielectric effects. The rest effect may therefore be associated with metal–ligand interaction, notably the bonding properties. Possible reasons for a large R factor are:

(i) The M–L bond length increases as the number of bound ligands increases. Thus, in the extreme case, the bonding could change from low covalent character in the first association stage to ionic character in the second. Such an effect was not noted in the α-hydroxymonocarboxylate systems listed in Table I, and it is unlikely to be present here. Bjerrum (2) has shown that the M–L bond length does not change upon higher association for simple nitrogen-bonding ligands.

(ii) The ligand is bidentate in the first association stage and monodentate in the second. This possibility has been eliminated earlier in this work.

(iii) The metal–ligand bond is sufficiently covalent that considerable charge is transferred from ligand to metal. The electrostatic attractive force between metal and ligand in the second association stage is then reduced. The greater the covalency of the metal–ligand bond the greater will be R. Copper–oxygen bonds would seem to be mainly ionic, however, as the Cu–glycolate data in Table I show (T = 1.6). Covalent bonding can therefore be attributed to Cu–N bonds. The magnitude of R shows that the order of metal–ligand covalency for (primary amino) amino acid systems is

Cu > Ni: > Co > Fe ≡ Zn ~ O. This series is in accord with the deductions of Martell and Calvin (4) from the slopes of plots of the second ionization potential of the metal against complex stability, for different oxygen- and nitrogen-bonding ligands. While the R values could tell us, in principle, the amount of charge transferred to the metal (metal–ligand covalency), the calculation becomes impractical because of the unknowns associated with the M–L distance over which the continuous transfer of charge takes place. Let us assume that the transfer of charge occurs over a distance short compared with the equilibrium M–L bond length (r), i.e. the second ligand approaches the metal to a distance $r + \Delta r$, and charge is then transferred continuously over a distance Δr. If $\Delta r \ll r$, assuming that $\log T \alpha q_1 q_2$ (where q_1 and q_2 are charges on bound and unbound ligands) and $\log b \alpha e^2 \frac{e}{r}$ (e is net metal charge), the following values may be calculated for the net charge transferred from ligand to metal: Cu = 0.06, Ni = 0.04, and Co = 0.03. The Cu-N bond would seem to be ~ 3% covalent. The ready formation of e.g. $Ni\left(NH_3\right)_6^{2+}$, confirms the low covalent character of these M-N bonds.

P values for the (secondary amino) amino acids (Table IV) suggest that Cu–N covalency is small and R = 1.1. For Ni, however, the Ni–N bond would seem to be only slightly less covalent than in the primary amino system. It is possible that the more strongly acid oxygen atom of the (secondary amino) amino acid has similar bonding properties to the oxygen atom of water. The (secondary amino) amino acids are therefore capable of displacing all 6 waters of the Cu^{2+} primary hydration sheath

with equal facility. The N atom would bind in the square plane and the O atom either in the square plane or perpendicular to the square plane. For this model, S = 4.8, S x T = 7.7 and R = 1.8, corresponding to P(obs.) = 14. This R value is more consistent with that for Ni. Furthermore, for the Cu-$OOC.CH_2.N(CH_3)_2$ system (12), P(obs.) = 9, whereas for square planar bonding only, S = 8.0. For 6 available Cu sites, S x T = 7.7, giving an R value = 1.2. The R value for the Ni system is 1.4, since P(obs.) = 11. It would seem, therefore, that the secondary amino and tertiary amino amino acids can displace all 6 waters of the Cu^{2+} sheath.

Let us consider the halide systems. Published P, P_{23} ($= b_2:b_3$), and P_{34} ($= b_3:b_4$) values are listed in Table V, the values being those measured by Morris and coworkers (24-28). The results of these workers seem reliable. For example, the P values for the Mn, Co, and Zn chlorides average at 8.3 ± 0.6, while the P_{23} values for the Mn and Zn chlorides are also in excellent agreement.

The stabilities of Zn halide complexes follow the order chloride > bromide > iodide. This order indicates ionic bonding in these systems, since for covalent bonding the order is reversed (e.g. Cd, ref 29). Structural changes upon ion association can also markedly affect P values as is well observed in silver–ammonia reactions (22). This effect is of particular relevance in the present study, where, in the Co–chloride system, cation bonding changes from octahedral (hydrated ion) to tetrahedral (tetrachloro complex). A structural change in the n^{th} association stage will lead to a large $P_{n,\, n+1}$ value because of the favourable entropy change in

the n^{th} stage. Large $P_{n, n+1}$ values should therefore be a guide as to the stage of ion association at which the octahedral→tetrahedral change occurs. In the Ag^{+} – ammonia system (22), the P values are anomalously small because of the change from higher to lower coordination in the second association stage, probably from $Ag(NH_3)(OH_2)_{3 \text{ or } 5}$ to linear $Ag(NH_3)_2$.

The P values listed in Table V indicate that Mn, Co, and Zn react in similar fashion with chloride. The metal-chloride bonds would seem to be ionic. If the 1:1 halide complex is octahedral, i.e. replacement of a water by a halide, then S = 2 x 6/5 = 2.40, and using a T values = 1.6, P = 3.8. The P values for Ni–Cl and Zn–Br systems are in good agreement with this, indicating that the 1:1 complexes are octahedral. This is to be expected for the Ni system (22), and shows that a T value = 1.6 holds for yet another transition metal–singly–charged ligand system.

The P values for the Mn, Co, and Zn chlorides are considerably greater than 3.8. This would suggest, according to our earlier criterion, a structural change in the first association stage. Since Mn and Zn are d^5 and d^{10} ions, ligand field effects may be ignored. For Co, however, the P values will contain a contribution from the ligand field stabilization energy difference between the initial and final structures. If the 1:1 complexes are tetrahedral, then $S_{23} = 3/2 \times 3/2 = 2.25$. The separation of the bound ligands in a 1:2 complex is greater in a tetrahedral complex than in an octahedral. According to N. Bjerrum (23), $\log T \propto 1/r_1$, where r_1 is the equilibrium separation bound ligands. On this basis, a reasonable T value for tetrahedral orientation would be ~ 1.5. Hence, $P_{23}(\text{calc.}) \sim 3.3$,

which is in fair agreement with P_{23} (obs.) = 2.4. However, P_{34} (obs.) for the Zn–Cl system = 0.1, which suggests a structural change in the fourth association stage. A possible explanation of this would be that the higher chloride complexes are square planar and the 1:4, tetrahedral. This is unlikely in view of the rare occurrence of square planar complexes of these cations. For these weak complexes, errors in the determination of b_3 and b_4 could be large, and it may be unwise to place too great an emphasis on the interpretation of P_{34}. It is conceivable that the successive binding of halide ions renders the metal-water bond increasingly weaker, thus lowering the magnitude of $P_{n,\ n+1}$ values. We would favour the hypothesis that the transition from 6-coordination to 4-coordination (very likely tetrahedral) occurs in the first association stage for Mn, Co, and Zn chlorides. The P values would seem to be too large for a 5-coordinate 1:1 complex and a 4-coordinate 1:2 complex, since the ΔS values for the two ion association stages should be approximately equal. The 1:3 Co:Cl complex has been postulated as being tetrahedral (22).

The studies of Irish and coworkers (30) are pertinent at this point. Their Raman work failed to detect a 1:3 zinc chloride complex, which would confirm the small P_{34} value. Irish and co-workers (30) proposed that the 1:2 $ZnCl_2$ species was linear with four waters making up the octahedron, but this model demands that S = 2 x 6/1 = 12. Consequently, since P(obs.) < S, the 1:2 species cannot be linear. Further, the observed P values are not in accord with the octahedral $ZnCl_4(OH_2)_2$ structure also postulated by Irish and co-workers(30). The Raman works of Woodward and Nord (31) and

of Morris, Short and Waters (32) favour a tetrahedral structure for $ZnCl_4^=$.

The Cu^{2+} – chloride data are consistent with considerable charge transfer from ligand to metal in the first association stage, the electron being transferred from a ligand orbital to a metal antibonding orbital. This electronic transition is manifested by the absorption bands that occur in the U.V. region of the spectrum of cupric chloride solutions (33). The 1:1 Cu:Cl species in solution has an absorption band in its spectrum close to that of $Cu(OH_2)_6^{2+}$, indicating that 1:1 complex is octahedral (33). Hence, P(calc.) = 4/3 x 2 x 1.6 = 4.3, whereas P(obs.) = 18. Therefore, R ~4, which may be compared with the R factor for cupric–amino acid complexes (Table III). However, P_{23}(obs.) = 0.71, a value that would seem to indicate a change in cation coordination number. The magnitude of P_{34}(obs.) is also smaller than expected, which suggests a further change in coordination. It would seem reasonable to suggest that the 1:4 complex is tetrahedral and the 1:3 either tetrahedral or 5-coordinate. Mr. G. Faye (33), of this laboratory, has examined, spectrophotometrically, cupric chloride solutions in acetone, and has assigned absorption bonds at 950 mμ and 1125 mμ to 5-coordinate and tetrahedral species respectively. Tetrahedral $CuCl_4^=$ species have been observed in crystals (22), while a number of workers have postulated the formation of such complexes in aqueous solutions and in melts (34, 35). Barnes and Hume (36) have suggested that the 1:3 copper:bromide complex in Cu^{2+} – HBr solutions is 5-coordinate. Our analysis of the stability constant ratios would seem to favour a tetrahedral 1:4 cupric:chloride complex, but the 1:3 complex would

seem to be either tetrahedral or 5-coordinate.

CONCLUSION

Interpretations of the magnitudes of stepwise stability constant ratios for transition metal and zinc amino acid and halide complexes have led us to the following conclusions:

(a) The method is capable of giving reliable information on the nature of metal–ligand bond.

(b) Electrostatic repulsion between a bound ligand (in a M–L complex) and a potentially binding ligand contributes a factor ≈ 1.6 to the magnitude of the stepwise stability constant ratio, where L ≈ singly-charged ligand and M ≈ transition metal, Zn or rare-earth ion.

(c) M–N bond covalency follows the order Cu>Ni>Co>Mn ≈ Fe ≈ Zn~O.

(d) For the chloride complexes of Co, Mn, and Zn, a change in metal coordination from octahedral to tetrahedral occurs in the first association stage.

(e) $NiCl^+$ and $ZnBr^+$ are octahedral (5-hydrated).

(f) The M–Cl bond is ionic for M ≈ Co, Mn, Zn, and Ni, while charge transfer effects are present in the Cu system.

(g) The 1:4 copper:chloride complex is tetrahedral.

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PGM:vn

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TABLE I

T values for metal–ligand complexes

Metal	Ligand	Bonding	T
rare-earth	R´. CH (OH). COOH	monodentate	1.5 ± 0.25
Cu^{2+}	glycolate	bidentate	1.5 ± 0.3
Cu^{2+}	acetate	monodentate	1.75 ± 0.1
Zn^{2+}	mandelate	monodentate	1.5

R´ = organic group

TABLE II

LogP values for metal–ligand complexes

Ligand	Cu	Ni	Co	Fe	Mn	Zn
glycine	1.65	1.22	1.21	0.8	0.9	1.08
"	1.25	0.97	0.86		0.69	0.66
"	1.60	1.2	0.87			0.94
"	1.51	1.09	0.96			1.1
"	1.21	0.97	1.05			0.82
"	1.6	1.08	0.86			0.83
"			1.3			
alanine	1.04	1.26	1.16		0.43	0.82
"	1.65		0.82			0.88
"	1.53		0.88			
leucine	1.45		0.84		0.11	0.91
β-alanine	1.66	1.23				
α-NH_2but.			0.86			0.84
norvaline	1.58	1.25	1.22			0.99
valine	1.22		1.00		0.12	0.90
"	1.40		0.90			
Average P values	31	14	10	~6.5	6.5	8

Source of P values, references 5 - 19

TABLE III

R factors for metal–amino acid complexes

Factor	Cu	Ni	Co	Fe	Mn	Zn
P(obs.)	31	14	10	~ 6.5	6.5	8
S	8.0	4.8	4.8	4.8	4.8	4.8
T	1.6	1.6	1.6	1.6	1.6	1.6
P(calc.)	12.8	7.7	7.7	7.7	7.7	7.7
R	2.4	1.8	1.3	~1	~1	1.0

TABLE IV

LogP values for Cu and Ni complexes

Ligand	Cu	Ni
iso - $C_3H_7.NH.CH_2.COOH$	0.95	
$C_4H_9.NH.CH_2.COOH$	1.12	1.14
n - $C_3H_7.NH.CH_2.COOH$	1.19	1.12
$CH_3.NH.CH_2.COOH$	1.29	1.12
$C_2H_5.NH.CH_2.COOH$	1.13	1.08
Average obs. P value =	14	13
P(calc.)	12.8*	7.7

Source of P(obs.) values, reference 12.

* Calculated for four available cation sites.

TABLE V

$P_{n, n+1}$ values for metal–halide complexes

Ligand	$P_{n, n+1}$	Cu	Ni	Co	Mn	Zn
Cl	P	19	3.2	7.4	8.3	9.3
	P_{23}	0.7			2.0	2.8
	P_{34}	2.5				
Br^-	P					3.5

Source of $P_{n, n+1}$ values, references 24-28.